Turning the red mist of carbon dots into red-carpet for photocatalysis

Carbon dots (CDs) are nanoparticles typically <20 nm in size, first discovered in 2004 as a by-product during the electrophoretic purification of carbon nanotubes. Since then, CDs slowly began to gain more and more research attention until 2008 when the first bottom-up CDs were described, leading to a very rapid increase in publications on the synthesis and properties of these nanomaterials. It became a natural step in the development of these materials to seek to obtain CDs showing red-shifted fluorescence. In the case of carbon dots derived from citric acid, this goal was achieved in 2016, paving the way for these materials in advanced biological applications such as two-photon imaging, photodynamic and photothermal therapy. Despite the myriad potential practical applications of red-emitting CDs, some fundamental aspects regarding their chemical structure and the source of their intriguing photophysical properties still await clarification. Currently, it is the lack of a complementary understanding of structure-property correlations that seems to be the biggest barrier limiting the rational design and, above all, further development of these materials. At first glance, overcoming this obstacle seems easy, however, given the great variety of substrates used for synthesis, reaction conditions and purification methods on the one hand, and the number of CD fluorescence mechanisms proposed in the literature on the other - the situation becomes more complicated. With this in mind, the primary objective of this project is to formulate a coherent methodology (roadmap) aimed at the preparation of new nanomaterials for photocatalysis applications based on red fluorescent carbon dots, their molecular fluorophores, as well as special micelles prepared from these fluorophores. The above objective is planned to be achieved through a number of sub-objectives.

As a first step, it is planned to develop structures of red and orange emitting fluorophores formed in situ during CD synthesis. Thus, different CDs will be prepared by systematically evolving the synthesis methods presented in the literature until suitable conditions for the separation of the dyes are achieved. Then, the red and orange emitting fluorophores will be isolated, their structures will be elucidated and their basic photophysical properties will be characterised and compared with the corresponding CDs. Subsequently, the obtained fluorophores will be used to prepare specific amphiphilic derivatives, which in turn will be converted into micelles in a further procedure. Finally, the suitability of all the materials obtained (molecular fluorophores, CDs and micelles) will be evaluated in photocatalytic processes for the preparation of hydrogen from water.

It is assumed that following the proposed scheme will allow the principles governing the emission of light from ‘red’ CDs to be known, enable their design and further development, and allow materials useful in photocatalysis to be obtained.

In conclusion, the aim of the project is not only to point out the ‘mistakes of youth’ of carbon dots, but first and foremost to answer the much more challenging question of ‘what to do to make the carbon dot great again?’.

The project may result in the development of a methodology for obtaining carbon nanomaterials with the designed optical properties. In addition, as a result of the activities planned in the project, it will be possible to understand the mechanisms governing the emission of light from these intriguing nanomaterials, which will undoubtedly contribute to the development of fundamental knowledge and may have tangible application benefits in applications such as bioimaging, photodynamic therapy or the photocatalytic production of hydrogen from water.